THE UNIVERSITY of EDINBURGH

Edinburgh Research Explorer

Pyrolysis characteristics of waste tire particles in fixed-bed reactor with internals

Citation for published version:
Xu, S, Lai, D, Zeng, X, Zhang, L, Han, Z, Cheng, J, Wu, R, Mašek, O & Xu, G 2018, 'Pyrolysis characteristics of waste tire particles in fixed-bed reactor with internals', *Carbon Resources Conversion*. https://doi.org/10.1016/j.crcon.2018.10.001

Digital Object Identifier (DOI):
10.1016/j.crcon.2018.10.001

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Peer reviewed version

Published In:
Carbon Resources Conversion

Publisher Rights Statement:
© 2018 Production and hosting by Elsevier B.V. on behalf of KeAi Communications Co., Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/BY-NC-ND/4.0/).

General rights
Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

OPEN ACCESS

Download date: 06. May. 2023

ARTICLE IN PRESS

Carbon Resources Conversion xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Carbon Resources Conversion

journal homepage: http://www.keaipublishing.com/en/journals/carbon-resources-conversion

Pyrolysis characteristics of waste tire particles in fixed-bed reactor with internals

Shipei Xu[a,c], Dengguo Lai[a,c], Xi Zeng[a], Lijuan Zhang[a], Zhennan Han[b], Jiguang Cheng[b], Rongcheng Wu[a], Ondřej Mašek[d], Guangwen Xu[b,*]

[a] State Key Laboratory of Multi-phase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
[b] Institute of Industrial Chemistry and Energy Technology, Shenyang University of Chemical Technology, Shenyang 110142, China
[c] University of Chinese Academy of Sciences, Beijing 100049, China
[d] University of Edinburgh, Edinburgh EH9 3FF, Scotland, United Kingdom

HIGHLIGHT

- An innovative fixed bed reactor with internals was employed to pyrolyze waste tire particles.
- Pyrolysis of waste tire particles has much higher rate of volatile generation than pyrolyzing coal.
- Using internals doubled heating efficiency to in-bed waste tire particles and enabled higher pyrolysis oil yield.
- Using internals suppressed secondary reactions to volatile and reduced N and S contents in pyrolysis oil.

ARTICLE INFO

Keywords:
Pyrolysis
Waste tire
Fixed bed
Internals
Secondary reactions

ABSTRACT

This study investigated the characteristics of pyrolysis for waste tire particles in the newly developed fixed-bed reactor with internals that are a central gas collection channel mounted inside reactor. And a few metallic plates vertically welded on the internal wall of the reactors and extending to the region closing their central gas collection pipe walls. Experiments were conducted in two laboratory fixed bed reactors with or without the internals. The results shown that employing internals produced more light oil at externally heating temperatures above 700 °C due to the inhibited secondary reactions in the reactor. The oil from the reactor with internals contained more aliphatic hydrocarbons and fewer aromatic hydrocarbons, leading to its higher H/C atomic ratios as for crude petroleum oil. The char yield was relatively stable for two beds and showed the higher heating values (HHVs) of about 23 MJ/kg. The gaseous product of pyrolysis mainly consisted of H_2 and CH_4, but the use of internals led to less pyrolysis gas through its promotion of oil production.

1. Introduction

In recent years, waste tires have become a serious environmental problem because of the increasing amounts generated (globally over 1 billion waste tires per year). Waste tires are difficult to be biologically degraded [1–3], have high risk to incur fire and release uncontrollable harmful compounds or elements [4,5]. On the other hand, due to high calorific value and high content of rubber and carbon black, waste tires can be considered as an important and available resource to be fuel or raw material for production of high valuable chemicals [6–8]. Up to now, many technical ways have been researched and developed, as shown in Table 1, to utilize waste tires. Among them, tire renovation and rubber recycling appear to have low environment risks and high economic values, but they are less suitable for low-quality tires and tires of different types. Theoretically, incineration for cement production can treat all types of waste tires, but this wastes the high-value components containing in tires and can lead to emissions of hazardous polycyclic aromatic hydrocarbons (PAHs). Compared to these mentioned technical ways, pyrolysis has been widely recognized as a promising and attractive utilization technology for waste tires. It is feasible nearly for all kinds of tires and allows effective production of oil, fuel gas and black carbon as fuel or material in large scale. However, efforts are required to control the possible pollution due to sulfur compounds generated during pyrolysis for oil and gas products.

According to their differences in heating rate, the reactors adopted for pyrolysis of waste tires can be classified into two groups, fast

* Corresponding author.
E-mail address: gwxu@ipe.ac.cn (G. Xu).

https://doi.org/10.1016/j.crcon.2018.10.001
Received 20 July 2018; Received in revised form 23 August 2018; Accepted 23 October 2018
2588-9133/ © 2018 Production and hosting by Elsevier B.V. on behalf of KeAi Communications Co., Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/BY-NC-ND/4.0/).

Please cite this article as: Xu, S., Carbon Resources Conversion, https://doi.org/10.1016/j.crcon.2018.10.001

Table 1
Major technical ways to recycle waste tire.

Technical ways	Advantages	Disadvantages
Renovating tire	High economic value and less harmful to environment.	Suitable only high-quality (natural) fresh tire.
Making rubber powders	High economic value and simple process.	Limited uses of powder product and relatively high processing pollution.
Incineration	Wide application for all tires as alternative energy.	Low economic value and wasting the high value of rubber as material.
Cement production	For all tires to replace coal and with low investment by using existing facilities.	Low economic value and wasting the high value of rubber as material.
Pyrolysis	Applicable to all tires and high economic values.	Controlling pollution due to S in oil and char from waste tires.

pyrolysis reactor and slow pyrolysis reactor [8,9]. For the former, it mainly includes fluidized bed [10] and plasma reactor [11]. Due to the high heat transfer rates and uniform temperature distribution in the fast pyrolysis reactor, the yield of oil is relatively high. On the other hand, the oil quality is often poor, due to the high contents of dust and heavy components present in the oil. The slow-pyrolysis reactors include fixed bed [12,13], moving bed [14] or rotary kiln [15]. Although this way is widely adopted because of its simple reactor structure, easy operation and low investment, some obvious limitations also exist to cause its low oil yield, difficulty for scale-up and limitation in treatment capacity in a single pyrolysis unit.

Recently, a fixed bed pyrolyzer with newly developed internals has been proposed and designed by Institute of process engineering, Chinese Academy of Sciences. The effect of these internals on pyrolysis of coal have been reported by Zhang et al. [16,17] in previous studies. These studies examined the pyrolysis behavior of coal by laboratory experiments and model tests in batch-type pyrolyzers at capacities of 1 kg and 100 kg, respectively. Both the tests well verified the technical features and superiorities in enhancement of heat transfer and improvement on oil yield and quality through adopting the designated internals. Lin and Siramard et al. [18,19] adopted this new pyrolysis reactor to treat oil shale, also achieving good results in high oil yield and good oil quality. Using a moving bed reactor with a capacity of 6 kg oil shale per hour, Lai et al. [20,21] further tested the use of internals for high-yield production of high-quality shale oil via solid-carrier pyrolysis. All such studies successfully demonstrated that the adoption of internals in pyrolyzers considerably enhanced heating rate in fixed / moving bed reactors indirectly heated and well regulated the flow of volatile product inside the pyrolyzer to form an internal gas flow from high to low temperatures. These consequently ensure the high yield of pyrolysis oil even at temperatures above 1000 °C and low dust content in the produced oil by an in-bed dust filtration effect due to the lateral flow of released volatile through the particle bed.

This work is devoted to extending the application of such a new pyrolysis reactor with internals to waste tire particles for the production of oil or other high-value chemicals. In order to show the technical distinctiveness of the pyrolysis reactor with internals, the same fixed bed reactor with and without internals were adopted in experiments and the results obtained were then compared. The work also tested the effect of pyrolysis (or heating furnace) temperature on product distribution and composition of oil, char and gas, whereby hoping to facilitate the application development of the reactor for pyrolyzing waste tire particles.

2. Experimental

2.1. Facility and procedures

Fig. 1 shows a schematic diagram of the adopted experimental system, mainly including its heating system, reactor, pyrolytic oil-gas separation system and gas cleaning and sampling system. Two fixed bed reactors without internals (A) and with internals (B) were adopted, and both were made of stainless steel with an inner diameter of 100 mm and an effective volume of 1900 mL. The internals mounted in reactor B consisted of several metallic plates and a central gas collection pipe. The metallic plates were adopted to enhance the heat transfer from reactor wall to waste wire particles in the bed, which were welded perpendicularly to the reactor wall and the plates were uniformly distributed in the cross-section of the reactor. Each plate had the size of 35 mm in length and 120 mm in height. The central gas collection pipe of 3 mm in diameter was a wall-punched metallic pipe located at the center of the pyrolyzer and connected to the reactor exit. The purpose of the pipe was to control the flow direction of formed volatile in the pyrolyzer, [19,22]. Both reactors were heated by an external electric furnace (5 KW). Silica wool was used to cover the interstice between furnace and the heated reactor at the top side to reduce the heat loss and maintain a uniform heating of the reactor.

Before each experiment, the pyrolyzer was filled with approximately 800 g of waste tire particles that had particle sizes below 5 mm, and it was in hen connected to the downstream separation and cleaning systems. When the furnace was heated to a preset temperature, the reactor for test (either with or without internals) was quickly put into the furnace to start the pyrolysis experiment. All recorded temperatures were measured using K-type thermocouples and automatically saved into a computer. A thermocouple at the center of reactor A or nearby the gas collecting pipe for reactor B measured the reaction temperature which was adopted to judge the ending time for all pyrolysis tests. At the end of heating or test, the reactor was quickly taken out from the furnace to terminate the pyrolysis reaction and to cool the reactor. Because the temperatures in the adopted reactor varied with position and time, in this work the data of pyrolysis were presented by correlating them with the temperature of the heating furnace.

In the downstream, a water-cooling pipe was connected to the reactor exit to rapidly cool down the evolved oil-containing hot pyrolysis gas and thus separate the oil and non-condensable gas [18]. In order to recover oil completely, a series of adsorbing bottles filled with acetone were used to scrub the gas stream leaving the water-cooling pipe. The cumulative volume of non-condensable gas was measured in a wet gas flow meter. After further removing sulfur and moisture behind the gas meter, the non-condensable gas was sampled using gas bags for analysis of the gas composition in an off-line micro GC (Agilent 3000).

2.2. Material and analysis

Table 2 shows the results of proximate and ultimate analyses for the tested waste tire particles. The tire rubber particles had relatively high volatile content of up to 62 wt % (air-dry base). The particle sizes of the tested waste tire were below 5 mm, and Table 3 shows the detailed size distribution. Thermogravimetric (TG) analysis was conducted using a LabSYS evo TG in Argon atmosphere with a flow rate of 200 mL/min and at a heating rate of 4 °C/min. Fig. 2 shows the results from TG test of the waste tire sample. The main mass loss occurred in the temperature range of 350–500 °C, and above 500 °C there was almost not any pyrolysis reaction. Hence, the suitable pyrolysis temperatures for producing oil can be below 500 °C.

After each experiment, the cooled char was weighed and the connection pipe from the reactor outlet to the adsorbing bottle was washed using acetone. The collected washing liquid was mixed with that from

ARTICLE IN PRESS

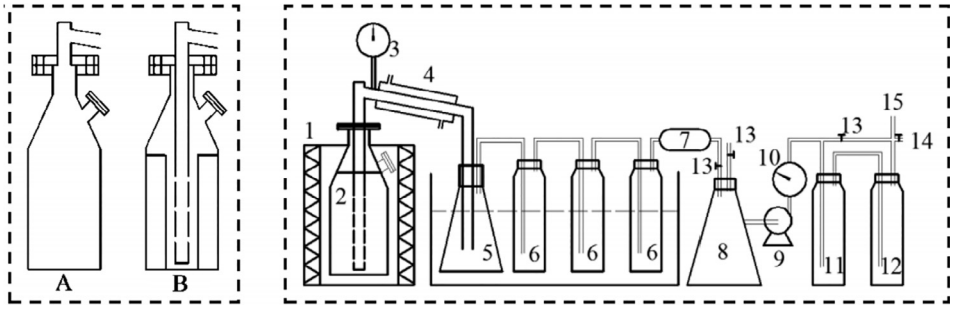

Fig. 1. Schematic diagrams for the tested fixed-bed reactors A (without internals) and B (with internals) and the adopted experimental system (1. Furnace; 2. reactor; 3. pressure gauge; 4. condenser; 5. collection bottle; 6. acetone scrubbing bottle; 7. filter; 8. buffer flask; 9. vacuum pump; 10. wet gas meter; 11. sodium bicarbonate washing bottle; 12. silica gel column; 13. valve; 14. gas sampling; 15. exhaust).

Table 2
Proximate and ultimate analyses for the tested waste tire particles.

Proximate analysis (w_{ad}%)				Ultimate analysis (w_{daf}%)				
M	V	A	FC	C	H	N	S	O[a]
1.22	62.36	6.97	29.45	88.44	7.40	0.61	1.50	2.05

[a] By difference.

Table 3
Particle size distribution of the tested waste tire material.

Particle size (mm)	0–1	1–3	3–5
Weight percentage (%)	35.3	34.3	30.4

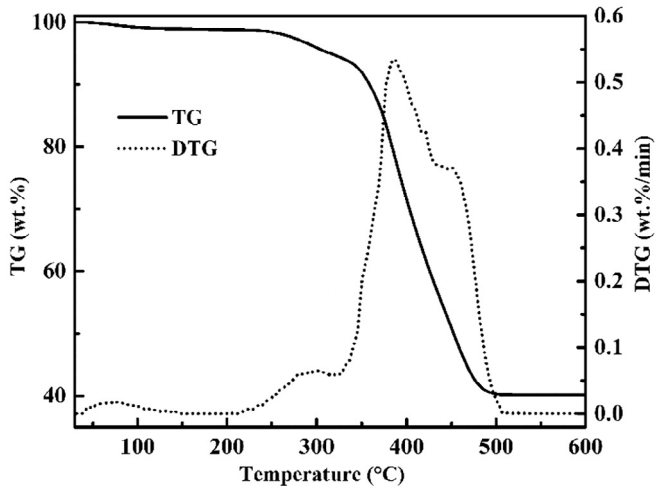

Fig. 2. Results of TG/DTG analysis for the tested waste tire particles.

the adsorbing bottles and further treated using rotary evaporation at 25 °C and −0.9 atm. to remove acetone and to get oil. This oil was mixed into the water-containing oil collected by the water-cooling pipe. The mixed oil was further weighted, and its moisture content was measured using the toluene azeotropic method to get the dry-base oil amount [18]. The yields of pyrolysis products, as Y_{char}, Y_{oil}, Y_{water} and Y_{gas}, were calculated from their absolute masses with respect to the mass of initial waste tire particles as raw material of pyrolysis.

The distribution of oil distillates was obtained from a high-temperature gas chromatograph (Agilent 7890A) following the simulated distillation method [19]. According to boiling points of obtained distillates, the obtained waste tire oil was divided into light oil, vacuum gas oil (VGO) and heavy oil for fractions with boiling points below 350 °C, in 350–500 °C and above 500 °C, respectively. The light oil fraction was further analyzed using a gas-chromatography mass-spectrometer (GC-MS, QP 2010 Ultra, Shimadzu) to get its detailed chemical composition information. The GC-MS worked with a sample injector and a detector running at 280 °C, and the heating rate to them was 6 °C/min and the analysis time at 280 °C was 10 minutes. The scanning range of MS was 20 to 900 m/z and the used solvent delay time was 1.7 min. Based on the results of proximate and ultimate analyses for the oil, its HHV (higher heat value in MJ/kg) was calculated using Eq. (5) [23]

$$HHV = 0.3149 \times C + 1.1783 \times H + 0.1005 \times S - 0.1034 \times O - 0.0151 \times N - 0.0211 \times Ash. \quad (5)$$

The sampled non-condensable pyrolysis gas (after passing a silica-gel column) was analyzed in a micro-GC (Agilent 3000A) to get its molar compositions of component gases H_2, CH_4, CO, CO_2 and CnHm (C_2H_4, C_2H_6, C_3H_6 and C_3H_8).

3. Results and discussion

3.1. Effect of internals

The temperatures inside the externally heated reactor are not uniform, and the temperature gradient in the reactor greatly varies with the heating rate as well as temperature of the external furnace. In this study the pyrolysis temperature shown hereafter refers to the one at the center of the reactor or near the central gas collection pipe wall. According to Fig. 2, the temperature terminating the waste tire pyrolysis in the fixed bed without or with internals can be determined to be 500 °C for such a pyrolysis temperature.

Fig. 3 shows the evolution of reaction temperature at the center of reactor A or nearby the wall of the gas collection pipe for reactor B. The furnace temperature for this comparison was 500, 550, 600, 700, 800 and 900 °C. As shown in all plots in Fig. 3. For both reactors, the temperature-rise curves (for the measured central point) can be divided into two stages, the drying stage below 110 °C and the pyrolysis stage from about 110 °C to 500 °C. Once the pyrolysis reaction began, the reaction temperature quickly increased, and gradually reached a constant value, namely the setpoint temperature. Generally, the higher the furnace setpoint temperature, the shorter the time needed for approaching the targeted reaction temperature at the central position because of the consequent stronger heat transfer at the higher heating (furnace) temperature. For example, at 500 °C the time needed was respectively about 170 and 65 minutes for reactors A and B, but at 900 °C they required only 38 and 26 minutes, respectively.

On the other hand, in comparison with reactor A without internals, the heating rate in reactor B with internals was clearly faster, leading to a shorter time needed for reaching the targeted reaction temperature at the monitored position. For example, at furnace temperature of 500 °C the time needed for reactor B to reach the setpoint temperature was only 39% of that for reactor A. Although the gap of heating time between the reactors A and B gradually declined with increasing the preset furnace temperature, it could still save about 40% of heating time at 900 °C for reactor B. All curves shown that adopting this particular design of reactor internals in a fixed bed reactor dramatically enhanced the heat transfer from the reactor wall to reactor center through the waste tire particles bed. This is due to not only the bigger heating surface provided by the plate internals but also the change of

ARTICLE IN PRESS

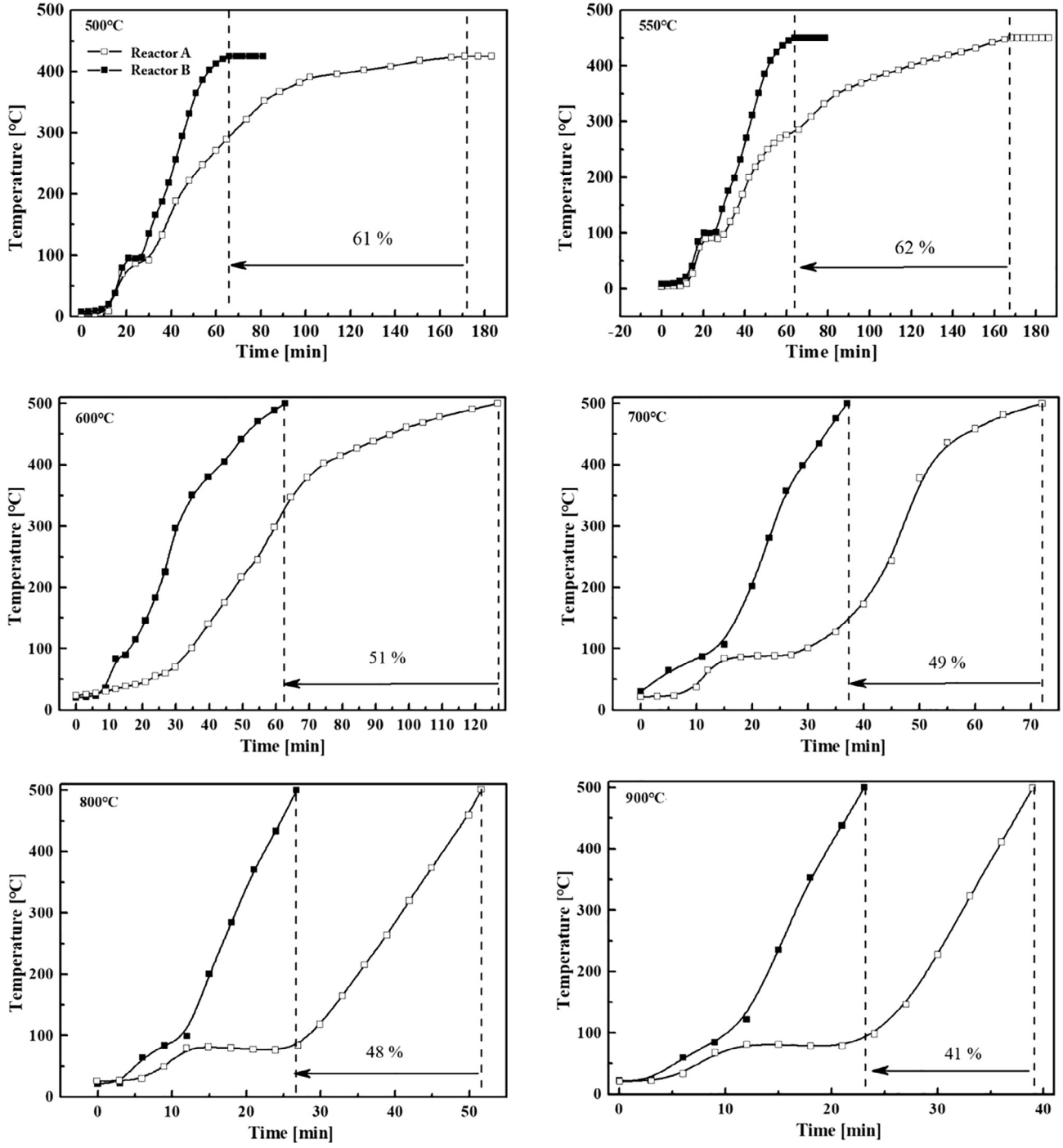

Fig. 3. Heating curves at the center (without internals) or near the wall of the central gas collection pipe (with internals) at two typical heating furnace temperatures.

heat transfer direction. In reactor B, the adopted internals including a few metallic plates and a central gas collection pipe promoted the heat transfer from the wall to the center of the reactor. The metallic plates, which connected with the wall of the reactor, transferred more heat and created more high temperature surfaces inside the reactor, because of the higher heat conductivity of the metallic plates. Although the central pipe did not contact the heated reactor wall, it varied the flow directions of the pyrolysis products. Instead of a radial flow to the annulus in reactor A, the pyrolysis products in reactor B were channeled to flow towards and into the central gas collection pipe. This product gas flow carried heat from the outside to the inner layer of low-temperature tire particles in the bed. The gas flow thus heated the tire particles in the inner layer of the bed. Thus, the enhancement of heat transfer by the metallic plates is via both its increase of heating area inside the bed, and channeling of hot volatiles and gases to flow through the low-temperature bed zones.

3.2. Product distribution

Fig. 4 shows the pyrolysis characteristics of waste tire particles at different furnace temperatures in reactors with and without internals. For both reactors the product distribution curve can be divided into two stages between temperatures of 500 °C and 900 °C, the low-temperature stage (LTS) below 600 °C and high-temperature stage (HTS) above 600 °C. In LTS, increasing furnace temperature released more volatile to increase the yields of oil and pyrolytic gas and to decrease the char

ARTICLE IN PRESS

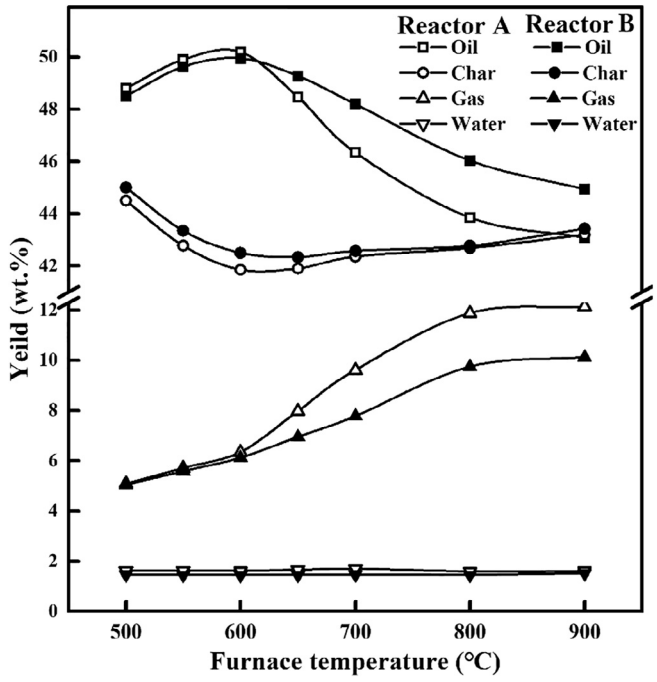

Fig. 4. Product distribution for pyrolyzing waste tire particles in the reactors A and B at heating furnace temperatures varying from 500 to 900 °C.

yield. At 600–900 °C of HTS, raising the furnace temperature led to a relatively stable char yield of 42.61wt % especially after 700 °C, while the oil yield sharply decreased and pyrolytic gas yield obviously increased. This shows in fact the cracking of oil which contributed to the gas yield and also deposited certain carbon on the char particles. Comparing with yield variation for reactor A without internals, the use of internals in reactor B lowered the decreasing rate in oil yield at temperatures above 700 °C. This shows that the internals in reactor B still suppressed secondary reactions to its produced oil inside the reactor.

Our previous studies on pyrolysis of coal and oil shale show that the installation of the mentioned internals for reactor B can not only shorten the heating time for the particle bed but also elevate the oil yield at temperatures even up to 1000 °C [16–22,24–26]. It is suggested that the added central gas collection pipe enabled all or almost all the formed gases and volatiles to flow into the low-temperature central pipe thus suppressing the secondary reactions (for coal and oil shale). Otherwise, in the absence of internals, the formed volatiles flow into the annular zone of the bed undergoing secondary reactions resulting in decreased oil yield with raising heating furnace temperature, as shown for reactor A in Fig. 4. This is because the char layer is always more porous than the layer of material particles does, because of more pore structure in the pyrolysis char [18,22]. For the pyrolysis of tire particles shown in Fig. 4, its oil yield for reactor B with internals still decreased with raising the heating furnace temperature after 700 °C. The phenomenon indicates that a part of formed volatile inside the reactor is likely to have flown backwards into the high-temperature annular zone of the bed undergoing secondary reactions in the annulus.

The possible reason is that for our tested reactor and conditions, the volatile formation rate (for waste tire particles) is higher or the suction-induced low pressure in the central flow pipe is insufficient to take all the formed volatile to make it fully flow into the pipe and then to the reactor exit. Indeed, the volatile content of waste tire particles is 62.36 w_{ad}%, almost two times of our previously tested coal (31.32 w_{ad}%) and oil shale (31.74 w_{ad}%). The temperature range for pyrolyzing tire particles is 250–500 °C in the TG diagram of Fig. 2, which is also lower than those for coal and oil shale particles. Hence, the volatile formation rate for pyrolysis of waste tire particles is surely much higher than those for pyrolysis of coal and oil shale particles. When using the same reactor and taking the similar testing conditions (especially the low pressure in the central pipe), there should be more volatile flowing into the high-temperature annulus of the reactor when pyrolyzing waste tire particles.

Table 4
Generation rates of volatile for different materials in reactor B at 900 °C.

Material	Feed weight (g)	Pyrolysis time (min)	Oil yield (wt %)	Gas yield (wt %)	Generation rate of oil (g/min)	Generation rate of volatile (g/min)
Tire	800	23	44.93	10.12	15.63	19.15
Coal	1300	44	10.34	9.99	3.06	6.01
Oil shale	1500	38	10.23	7.45	4.04	6.98

Table 4 further compares the releasing rate of oil and volatile for pyrolysis of waste tire, coal and oil shale. One can see that, for a specified reaction time under the same pyrolysis conditions (900 °C, using reactor B), the releasing rates of oil and volatile from waste tire particles are the highest by reaching 15.63 g/min and 19.15 g/min, respectively. These rates are three times higher than those for coal and oil shale particles. The result verified that the generated high-temperature gaseous volatile for tire particles should not completely escape the reactor as the volatile product did when pyrolyzing coal and oil shale particles in our previous studies. However, we believe the similar tendency of increasing oil yield with raising heating furnace temperature for pyrolysis of coal, oil shale and waste tire particles in the reactor with our designed internals. We are thus continuing our study of this issue by using the optimized reactor and experimental conditions.

3.3. Characterization of pyrolysis oil

Fig. 5 shows the evolution with furnace temperature of oil composition obtained from simulated distillation by high-temperature gas chromatograph for reactors A and B. Concerning reactor A, increasing temperature till 700 °C greatly decreased the fraction of light oil, while the content of vacuum gas oil (VOG) quickly increased. Above 700 °C,

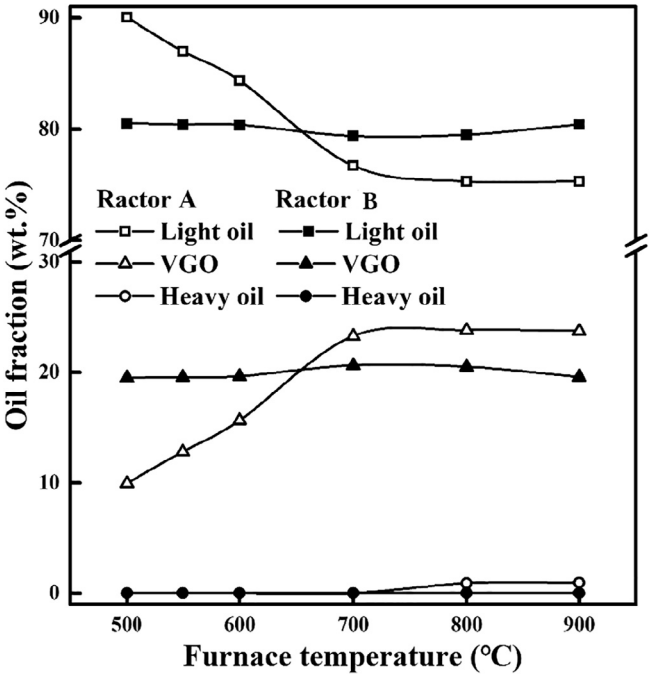

Fig. 5. Composition of oil obtained by pyrolyzing waste tire particles in the reactors A to B at heating furnace temperatures of 500 to 900 °C.

both of them became stable. For reactor B, the contents of light oil and VOG were almost constantly kept at the tested temperatures, indicating that its oil composition was not sensitive to the heating furnace temperature. The result complies with the processes in reactor B where formed volatiles flow into the low-temperature central gas collection pipe and do not experience serious secondary reactions at any heating temperatures.

Compared to reactor A without internals, the content of light oil for reactor B was clearly higher at furnace temperatures above 700 °C, while its content of VOG was lower for reactor B. Below 600 °C, the oil from reactor A had conversely higher light oil content but lower VGO content. This reveals that even below 600 °C, there were still certain secondary reactions occurring to the oil components present in the hot zone nearby the reactor wall. The secondary reactions would convert light oil into VGO through formation of conjugated bonds [24]. At rather higher heating temperatures (above 700 °C), the secondary reactions to volatile became more pronounced so that more light oil components were cracked into gas to cause the lower light oil contents for reactor A than for reactor B. Hence, at the heating temperatures of 700 °C, 800 °C and 900 °C, the light oil contents were 76.7%, 75.3% and 75.3% for reactor A but 79.4%, 79.5% and 80.4% for reactor B, respectively. One would also note that there was no heavy oil component for reactor B even at furnace temperature as high as 900 °C. This implies that heavy components present in the formed volatiles were adsorbed on particles when they passed through the low-temperature particle bed surrounding the central gas collection pipe of reactor B. Because of this reactor B remains to have high oil yield and similarly good oil composition at all tested temperatures even up to 1000 °C.

Fig. 6 shows the GC-MS results of pyrolysis oils from reactors A and B. The plotted data refer to the percentage contents based on peak areas of aliphatic hydrocarbon, aromatic hydrocarbon, heteroatom compounds and limonene [18]. For reactor A, increasing the furnace temperature from 500 to 900 °C significantly decreased the content of aliphatic hydrocarbon from 50% to 35% (6(a)) but increased that of aromatic hydrocarbon from 31% to 50% (6(b)). The peak area percentage of heteroatom compounds did not change considerably above 500 °C, whereas that of limonene began to clearly decrease above 600 °C. For reactor B, the same rise in the furnace temperature significantly decreased the content of aliphatic hydrocarbons from 56% to 45% but increased the contents of aromatic hydrocarbon and heteroatom compounds from 29% to 35% and 16% to 20%, respectively. The content of limonene was relatively stable at all temperatures.

The oil from reactor B had a higher content of aliphatic hydrocarbon (44% to 56%) and a lower content of aromatic hydrocarbon (28% to 37%) than those from reactor A. The use of internals in reactor B reduced the Diels-Alder aromatization reaction that converts aliphatic hydrocarbon into aromatic hydrocarbon in high-temperature bed zone. Consequently, the pyrolysis oil in reactor B had the higher H/C atomic ratios, which are very similar to that of crude oil. Taking limonene as a token species of tire-pyrolysis oil, its concentration in the produced oil may largely impact the economic feasibility of waste tire pyrolysis process. Fig. 6(d) shows that the content of limonene was much higher at higher furnace temperatures for reactor B than for reactor A. Mkhize [27] reported that adopting higher heating rate did not improve total oil yield of waste tire particles pyrolysis but significantly improved the limonene yield. Therefore, the use of the designed internals for fixed / moving beds guarantees the high heating rates for high yields not only of total oil but also of limonene components. In addition, here we would like to reiterate that the use of the particularly designed internals develops also an effective in-bed filtration of dust carried with the formed volatile so that the recovered pyrolysis oil has very low dust contamination, as we have shown in our previous studies in pyrolysis of coal and oil shale.

Table 5 shows the results of ultimate analysis for pyrolysis oil of waste tire in two reactors at varied furnace temperatures. The C content was about 80 wt % and the H content was about 10 wt %. In both cases elevating furnace temperature slightly raised the content of C and decreased that of H. The atomic ratio of H/C in oils varied from 1.57 to 1.42 for reactor A and from 1.58 to 1.51 for reactor B corresponding to the rise of furnace temperature from 500 °C to 900 °C. Thus, the utilization of internals produced oils with slightly higher H content.

The contents of N and S in oil were respectively 0.6–0.9 wt % and 0.7–1.1 wt %, while the O content was 6.0–9.0 wt %. Raising furnace temperature increased the N and S contents and decreased the O content. The oil from reactor B had lower contents of S and N, and the difference in the N and S contents of oils from the two reactors was larger at higher furnace temperatures. At 900 °C the N and S contents were 0.89 wt % and 1.04 wt % for reactor A, and 0.73 wt % and 0.83 wt % for reactor B, respectively. At 500 °C such contents were respectively 0.73 wt % and 0.78 wt % for reactor A, and 0.64 wt % and 0.72 wt % for reactor B. Indeed, both N and S would mainly exist with cyclic compounds that are more in the produced oil from reactor A which suffers more severe secondary reactions toward oil. Table 5 shows further that the typical oil composition from reactor B at 900 °C was 10.33 wt % H, 82.02 wt % C, 0.73 wt % N, 0.83 wt % S and 6.09 wt % O. In comparison with crude oil, such a kind of pyrolysis oil has the similar atomic H/C ratio but higher N and O contents, possibly the S content is also higher. Thus, additional upgrading is required for utilization of waste tire pyrolysis oil as gasoline or diesel.

3.4. Analysis of solid char and pyrolysis gas

Table 6 presents the proximate and ultimate analyses of the produced char from pyrolyzing waste tire particles. Increasing furnace temperature deepened the degree of pyrolysis, which decreased the residual volatile content in the generated char from 12.01 wt % at 500 °C to 1.80 wt % at 900 °C for reactor A, and from 9.43 wt % to 2.41 wt % for reactor B (air-dry base). The fixed carbon content, on the contrary, increased from 74.37 wt % to 82.83 wt % for reactor A and from 74.34 wt % to 82.39 wt % for reactor B. Reactor type (A or B) did not have any clear effect on char volatile matter and fixed carbon contents. The char from pyrolysis of waste tire particles mainly consists of carbon black and additives (both are added in tire production process), and has also high thermal and mass stability. All chars had high ash content of 13–16 wt % and their O contents also remained high in a range of 13–20 wt %. Noting that rubber is basically hydrocarbons, and the O in tire particles should mainly come from inorganic additives. The decrease of O content in char with raising heating temperature shows that decomposition of such additives occurred at the tested higher pyrolysis temperatures.

The calculated HHVs of the obtained char did not vary much with the heating furnace temperature and had a value of about 24 MJ/kg. However, we should note that by removal of volatile the S content in the chars became higher than in the raw waste tire particles and reached about 3.0 wt%. The N content in the obtained chars was slightly lower than in raw material. Thus, pyrolysis removed more nitrogen from char in comparison with the removed S. The N content in char varied slightly with temperature, while the S content increased with raising temperature implying that N was easier to remove with volatiles than S. Because of its high C content, the waste tire char can be milled into powder to be used in many industries. On the other hand, it can also be activated to make activated carbon and used as pollutant adsorbents for gas and water treatments [28,29]. The ash from tire particles was concentrated from 6.97 wt % to about 16 wt % after pyrolysis, consisting mainly of zinc, silica and sulfur [1], as shown in Table 7. High ash content may negatively affect the activation efficiency of pyrolysis char [30]. On the other hand, the ash has a high content of ZnO, and it can be sublimated to produce ZnO as chemicals.

Fig. 7 compares the molar (volumetric) composition of pyrolysis gas at different heating furnace temperatures. All component gases showed their similar variations with temperatures for the reactors A and B. The dominant gas species are H_2, CH_4 and hydrocarbons C_mH_n (C_2 + C_3),

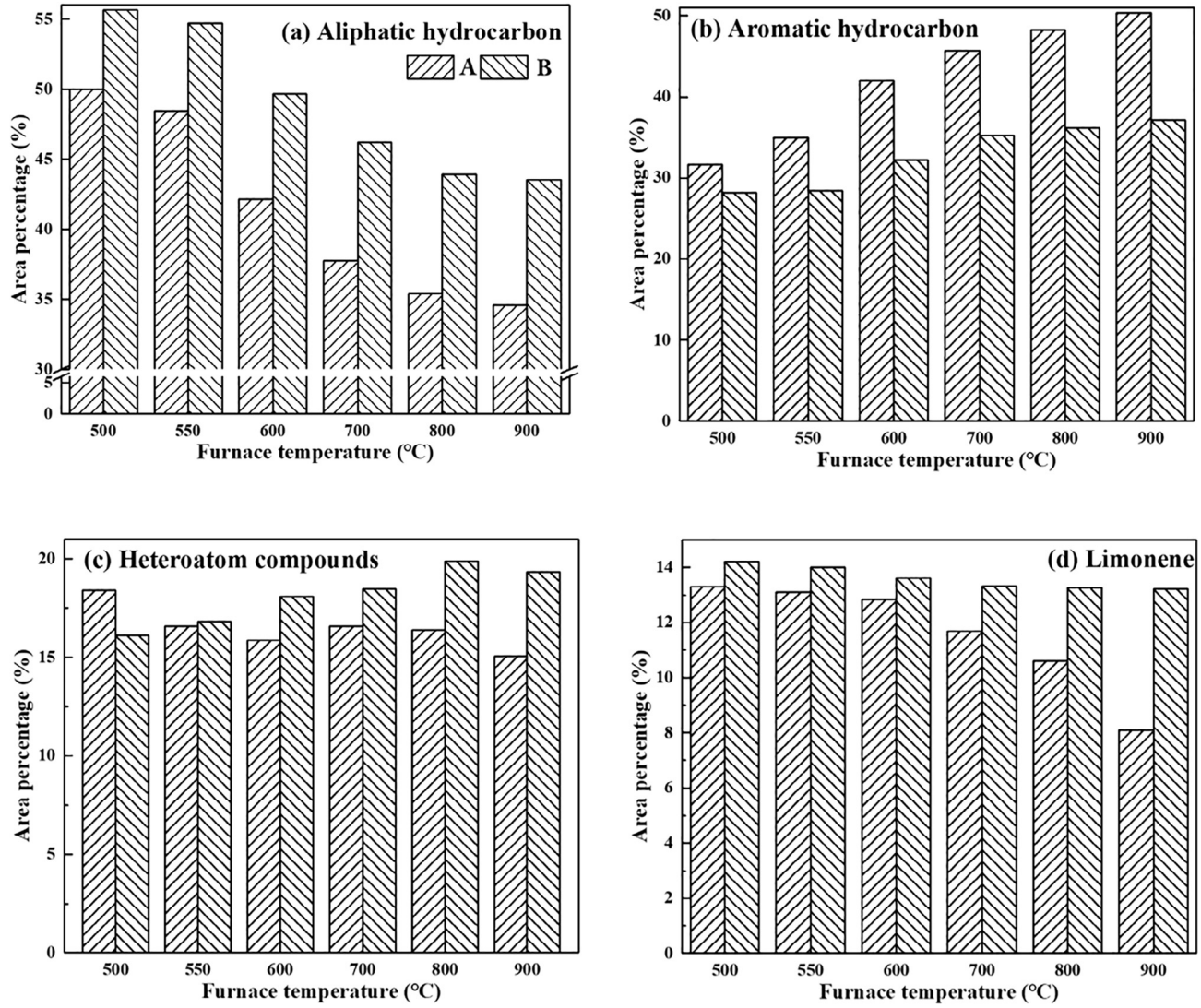

Fig. 6. Fractions of aliphatic hydrocarbon, aromatic hydrocarbon, heteroatom compounds and limonene obtained by GC–MS analysis of waste tire oils from pyrolysis in the reactors A and B at different heating furnace temperatures.

Table 5
Ultimate analysis of waste tire pyrolysis oil at different heating temperatures.

Reactor	Temperature (°C)	H	C	N	S	O[a]	H/C
A	500	10.45	80.04	0.73	0.78	8.00	1.57
	600	10.31	80.93	0.74	0.81	7.21	1.53
	700	10.21	81.42	0.74	0.82	6.82	1.50
	800	10.14	81.80	0.75	0.84	6.48	1.49
	900	9.94	82.11	0.89	1.04	6.02	1.42
B	500	10.52	79.83	0.64	0.72	8.29	1.58
	600	10.48	80.54	0.66	0.75	7.58	1.56
	700	10.45	81.33	0.68	0.78	6.76	1.54
	800	10.34	81.58	0.70	0.80	6.58	1.52
	900	10.33	82.02	0.73	0.83	6.09	1.51

[a] By difference.

which take about 90% of the produced pyrolysis gas in volume. The low CO and CO_2 contents in pyrolysis gas is the result of low O content in the rubber of waste tire particles, consisting predominantly of hydrocarbons without O. The formed CO_2 would be mainly from decomposition of inorganic additives, while the reaction of CO_2 with C led to certain formation of CO. Therefore, CO_2 content is always higher than CO in pyrolysis gas. Raising the furnace temperature from 500 °C to 900 °C increased the concentration of H_2 roughly from 35 vol% to 58 vol% but decreased the contents of CH_4 from about 31 vol% to 23 vol%, CO_2 from 10 vol% to 3 vol% and $C_2 + C_3$ hydrocarbons from 24 vol% to 12 vol%. This variation in pyrolysis gas composition demonstrates the higher degree of pyrolysis of rubber and also the increased cracking of oil into gas at higher furnace temperatures.

Fig. 8 further compares the concentrations of H_2, CH_4, $C_2 + C_3$, CO and CO_2 in pyrolysis gas products from the reactors A and B. The gas from reactor A had its higher contents of H_2 and $C_2 + C_3$ (C_mH_n) at all tested furnace temperatures, but at each temperature the concentration difference between two reactors are limited to 5 vol% and was slight at the furnace temperature of 900 °C. On the other hand, the gas from reactor B with internals had clearly higher CH_4 content, even by about 10 percent points at temperatures below 700 °C. The CO_2 and CO contents are also slightly higher, about 2 percent points, for the gas from reactor B.

Fig. 8 compares the yields of all gas components, showing that the pyrolysis in reactor caused higher yields for all other components except for CO_2. The yield of C_mH_n was distinctly higher for reactor A than for reactor B. Also, the higher heating furnace temperature caused the gas yield difference to be larger especially for CH_4, C_mH_n and H_2 as well. These characteristics in component gas yields and pyrolysis gas composition implied that more hydrocarbon oil species were cracked into C_mH_n, CH_4 and H_2 for the pyrolysis in reactor A. Indeed, in this

ARTICLE IN PRESS

Table 6
Proximate and ultimate analyses for chars from pyrolyzing waste tire particles.

Reactor	Tem. (°C)	Proximate anal. (w_d%)			Ultimate anal. (w_d%)					HHV (MJ/kg)
		V	A	FC	C	H	O[a]	N	S	
A	500	12.01	13.62	74.37	76.68	2.42	17.64	0.39	2.87	24.64
	600	5.58	15.81	78.61	78.83	1.51	16.30	0.38	2.98	23.16
	700	3.90	15.95	80.15	79.38	1.01	16.19	0.38	3.04	22.80
	800	2.39	15.51	82.10	79.52	0.84	16.09	0.36	3.20	22.82
	900	1.80	15.37	82.83	82.53	0.32	13.50	0.38	3.27	23.47
B	500	9.43	15.11	75.46	74.34	2.81	19.68	0.46	2.71	24.58
	600	3.91	17.18	78.91	75.14	2.69	18.91	0.45	2.82	22.59
	700	3.72	16.37	79.91	81.52	0.57	14.31	0.44	3.16	23.04
	800	3.24	15.42	81.34	81.95	0.50	13.98	0.40	3.18	23.41
	900	2.41	15.76	81.83	82.39	0.22	13.84	0.35	3.20	23.17

[a] By difference.

Table 7
Chemical composition of waste tire ash from char obtained by pyrolysis in reactor B with internals at a heating furnace temperature of 900 °C.

Composition	SiO_2	SO_3	ZnO	CaO	Al_2O_3	Na_2O	Fe_2O_3	MgO	K_2O	Others
wt%	40.86	15.93	13.39	12.63	6.66	3.68	2.86	2.16	1.08	0.76

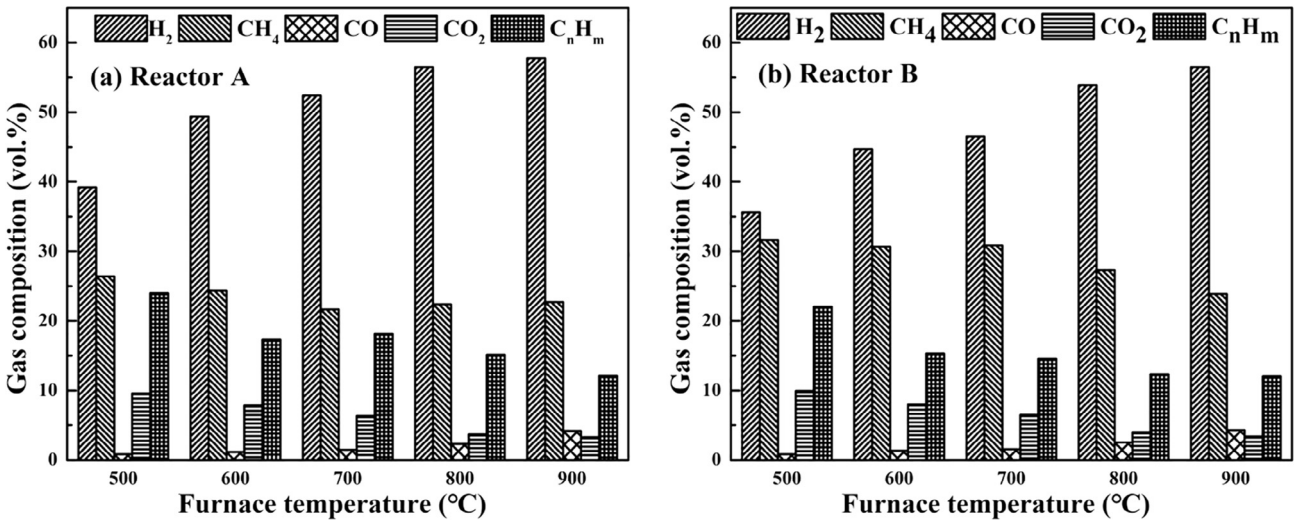

Fig. 7. Composition of waste tire pyrolysis gases from the reactors A and B at different heating furnace temperatures.

case all volatile components had to pass through the high-temperature wall zone of the reactor, therefore undergoing more extensive cracking reactions. In reactor B, only heavy species are adsorbed on low-temperature particles in the core zone, which then experience secondary cracking but at relatively lower temperatures (than in the wall region). Furthermore, the higher CH_4 content in pyrolysis gas for reactor B is likely to be due to the lower total gas volume produced. The lower CO_2 yield for reactor A means actually the occurrence of reforming reactions for high-C species by CO_2 in the high-temperature wall zone of reactor A. Corresponding to these features in composition, the HHV of pyrolysis gas is higher for reactor A because of its higher content of C_mHn and lower fraction of CO_2, as is shown in Fig. 8(f).

4. Conclusions

The study compared the pyrolysis performances of waste tire particles for production of oil and gas in two externally-heated laboratory fixed bed reactors mounted with and without our particularly designed internals consisting of a central gas collection pipes and a few metallic plates perpendicularly welded in the heated reactor. The pyrolysis was characterized at a given temperature of 500 °C measured at the reactor center or near the central gas collection pipe wall but for different external heating temperatures varying from 500 °C to 900 °C. The results showed that the adoption of internals in the fixed bed pyrolyzer not only increased the heating rate and shortened the heating time by over 40% but also enabled a higher oil yield, upto about 50 wt % of tire mass, by reducing the extent of secondary reactions such as cracking of produced volatile species. The char and gas yields of waste tire particles pyrolysis were respectively 40–50 wt % and 5–15 wt %, while the water generation was below 2 wt %.

Pyrolysis in the reactor with internals produced more light oil and less VGO and heavy oil at heating temperatures above 700 °C so that this oil had higher aliphatic hydrocarbon contents, lower aromatic hydrocarbon contents and higher H/C atomic ratios, comparable to crude oil. The utilization of internals also improved the yield of high-value limonene and reduced the contents of N and S in the produced pyrolysis oil of waste tire particles. The oil from waste tire pyrolysis contained about 82 wt % C, 10 wt % H, 6 wt % O, 0.7 wt % N and 0.8% S, showing the necessity of upgrading for using the oil as gasoline or diesel. The waste tire pyrolysis char particles contained about 80 wt % C, 16 wt % O and 3.0 wt % S, and had a HHV of about 23 MJ/kg, so it could be considered as a high-S fuel.

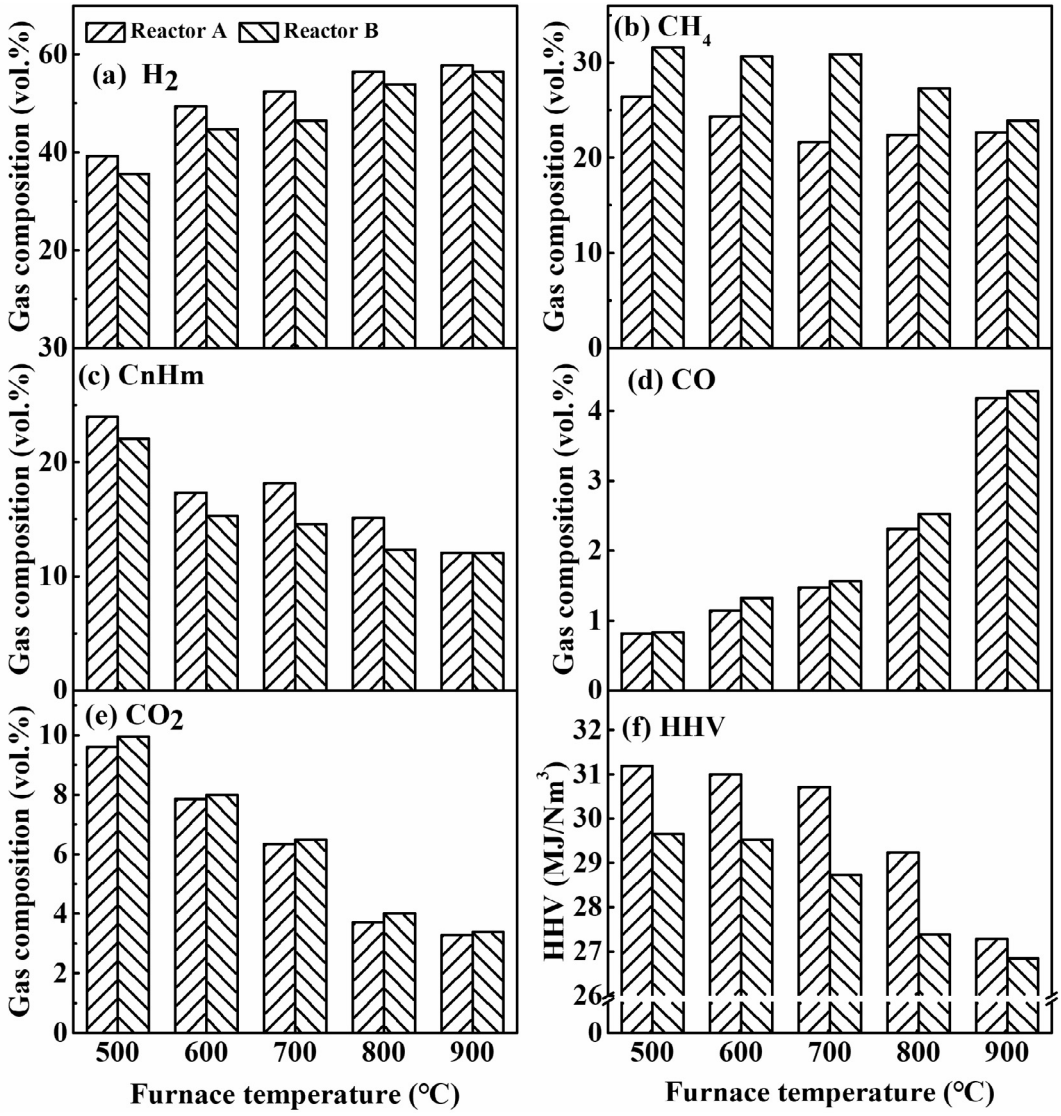

Fig. 8. Component gas concentrations of waste tire pyrolysis gases (a–e) and their corresponding heating values (f) for the reactors A and B at different heating furnace temperatures.

Between the two fixed bed reactor options, the gas yield was higher in reactor A, i.e. without internals, and increased with increasing pyrolysis temperature. The pyrolysis gas at a furnace temperature of 900 °C contains 50–55 vol% H_2, 20–25 vol% CH_4, 10–15 vol% $C_2 + C_3$ hydrocarbons and 3–5 vol% CO_2 as well CO, indicating the high quality of the produced pyrolysis gas. This reactor enabled higher yields of H_2, CH_4, C_mH_n and CO but slightly lower yield of CO_2 than the reactor with internals. This feature corresponds to the high oil yield for the reactor with internals. Thus, using internals in externally heated fixed bed reactors considerably suppressed secondary reactions (including cracking) occurring to volatile products in the reactor.

Acknowledgement

This study was supported by the National Basic Research Program of China (2014CB744303).

References

[1] G.G. Choi, S.H. Jung, S.J. Oh, J.S. Kim, Total utilization of waste tire rubber through pyrolysis to obtain oils and CO2 activation of pyrolysis char, Fuel Process. Technol. 123 (2014) 57–64.
[2] M. Hofman, R. Pietrzak, Adsorbents obtained from waste tires for NO2 removal under dry conditions at room temperature, Chem. Eng. J. 170 (2011) 202–208.
[3] M. Kyari, A. Cunliffe, P.T. Williams, Characterization of oils, gases, and char in relation to the pyrolysis of different brands of scrap automotive tires, Energy Fuels 19 (2005) 1165–1173.
[4] X. Zhang, T. Wang, L. Ma, J. Chang, Vacuum pyrolysis of waste tires with basic additives, Waste Manag. 28 (2008) 2301–2310.
[5] G. Lopez, J. Alvarez, M. Amutio, N.M. Mkhize, B. Danon, P. van der Gryp, J.F. Gorgens, J. Bilbao, M. Olazar, Waste truck-tyre processing by flash pyrolysis in a conical spouted bed reactor, Energy Convers. Manage. 142 (2017) 523–532.
[6] J.D. Martínez, N. Puy, R. Murillo, T. García, M.V. Navarro, A.M. Mastral, Waste tyre pyrolysis – a review, Renew. Sustain. Energy Rev. 23 (2013) 179–213.
[7] J.A. Conesa, I. Martin-Gullon, R. Font, J. Jauhiainen, Complete study of the pyrolysis and gasification of scrap tires in a pilot plant reactor, Environ. Sci. Technol. 38 (2004) 3189–3194.
[8] G. Lopez, M. Olazar, R. Aguado, J. Bilbao, Continuous pyrolysis of waste tyres in a conical spouted bed reactor, Fuel 89 (2010) 1946–1952.
[9] P.T. Williams, Pyrolysis of waste tyres: a review, Waste Manag. 33 (2013) 1714–1728.
[10] X. Dai, X. Yin, C. Wu, W. Zhang, Y. Chen, Pyrolysis of waste tires in a circulating fluidized-bed reactor, Energy 26 (2001) 385–399.
[11] H. Huang, L. Tang, Pyrolysis treatment of waste tire powder in a capacitively coupled RF plasma reactor, Energy Convers. Manage. 50 (2009) 611–617.
[12] P.T. Williams, S. Besler, D.T. Taylor, The pyrolysis of scrap automotive tyres: the influence of temperature and heating rate on product composition, Fuel 69 (1990) 1474–1482.
[13] A.M. Cunliffe, P.T. Williams, Composition of oils derived from the batch pyrolysis of tyres, J. Anal. Appl. Pyrol. 44 (1998) 131–152.
[14] E. Aylón, A. Fernández-Colino, M. Navarro, R. Murillo, T. García, A. Mastral, Waste tire pyrolysis: comparison between fixed bed reactor and moving bed reactor, Ind.

ARTICLE IN PRESS

Eng. Chem. Res. 47 (2008) 4029–4033.
[15] S.-Q. Li, Q. Yao, Y. Chi, J.-H. Yan, K.-F. Cen, Pilot-scale pyrolysis of scrap tires in a continuous rotary kiln reactor, Ind. Eng. Chem. Res. 43 (2004) 5133–5145.
[16] C. Zhang, R. Wu, E. Hu, S. Liu, G. Xu, Coal Pyrolysis for High-Quality Tar and Gas in 100 kg Fixed Bed Enhanced with Internals, Energy Fuels 28 (2014) 7294–7302.
[17] C. Zhang, R. Wu, G. Xu, Coal Pyrolysis for High-Quality Tar in a Fixed-Bed Pyrolyzer Enhanced with Internals, Energy Fuels 28 (2013) 236–244.
[18] L. Lin, C. Zhang, H. Li, D. Lai, G. Xu, Pyrolysis in indirectly heated fixed bed with internals: The first application to oil shale, Fuel Process. Technol. 138 (2015) 147–155.
[19] S. Siramard, L.X. Lin, C. Zhang, D.G. Lai, S. Cheng, G.W. Xu, Oil shale pyrolysis in indirectly heated fixed bed with internals under reduced pressure, Fuel Process. Technol. 148 (2016) 248–255.
[20] D. Lai, G. Zhang, G. Xu, Characterization of oil shale pyrolysis by solid heat carrier in moving bed with internals, Fuel Process. Technol. 158 (2017) 191–198.
[21] D. Lai, Y. Shi, S. Geng, Z. Chen, S. Gao, J.-H. Zhan, G. Xu, Secondary reactions in oil shale pyrolysis by solid heat carrier in a moving bed with internals, Fuel 173 (2016) 138–145.
[22] C. Zhang, R. Wu, G. Xu, Coal Pyrolysis for High-Quality Tar in a Fixed-Bed Pyrolyzer Enhanced with Internals, Energy Fuels 28 (2014) 236–244.
[23] S.A. Channiwala, P.P. Parikh, A unified correlation for estimating HHV of solid, liquid and gaseous fuels, Fuel 81 (2002) 1051–1063.
[24] D. Lai, Z. Chen, Y. Shi, L. Lin, J. Zhan, S. Gao, G. Xu, Pyrolysis of oil shale by solid heat carrier in an innovative moving bed with internals, Fuel 159 (2015) 943–951.
[25] L. Lin, D. Lai, Z. Shi, Z. Han, G. Xu, Distinctive oil shale pyrolysis behavior in indirectly heated fixed bed with internals, RSC Adv. 7 (2017) 21467–21474.
[26] S. Cheng, D. Lai, Z. Shi, L. Hong, J. Zhang, X. Zeng, S. Gao, G. Xu, Suppressing secondary reactions of coal pyrolysis by reducing pressure and mounting internals in fixed-bed reactor, Chin. J. Chem. Eng. 25 (2017) 507–515.
[27] N.M. Mkhize, P. van der Gryp, B. Danon, J.F. Görgens, Effect of temperature and heating rate on limonene production from waste tyre pyrolysis, J. Anal. Appl. Pyrol. 120 (2016) 314–320.
[28] J.F. González, J.M. Encinar, C.M. González-García, E. Sabio, A. Ramiro, J.L. Canito, J. Gañán, Preparation of activated carbons from used tyres by gasification with steam and carbon dioxide, Appl. Surf. Sci. 252 (2006) 5999–6004.
[29] E.L.K. Mui, D.C.K. Ko, G. McKay, Production of active carbons from waste tyres—a review, Carbon 42 (2004) 2789–2805.
[30] O.S. Chan, W.H. Cheung, G. McKay, Preparation and characterisation of demineralised tyre derived activated carbon, Carbon 49 (2011) 4674–4687.